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(54) METHOD OF PREPARATION OF LARGE CRYSTAL ALUMINOSILICATE
ZEOLITE CATALYST

(71) We, MOBIL OIL CORPORATION, a Corporation organised under the laws of the State of New York, United States of America, of 150 East 42nd Street, New York, New York 10017, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

This invention is directed to a method of preparing certain crystalline aluminosilicate zeolites wherein crystalline aluminosilicate zeolites of high purity are crystallized in the form of large particles having an ultimate crystal size greater than about one micron, that is from about 1 micron to 2 microns or larger. ZSM-5 catalysts having the above-described crystal size are highly useful in selective toluene disproportionation and methanol conversion processes and other selective aromatics conversion processes.

ZSM-5 crystalline aluminosilicate zeolites are well known in the art, being particularly described in U.S. Patent 3,702,886 and although large particle ZSM-5 type zeolites have previously been prepared, such processes have generally not been commercially viable procedures. It was previously thought that ultimate zeolite crystal size was predominantly dependent on the nature of the reaction mixture employed. It has now been discovered that crystal size is also significantly affected by the rate of addition of the organic compound, that is, its effective concentration in the crystallization media, and the temperature and pH conditions and the degree of agitation of the crystallization medium.

Accordingly, this invention is directed to a process for preparing a large crystal aluminosilicate zeolite catalyst which is characterised by having at least one crystalline dimension of at least 1 micron, and preferably from 1 to 2 microns or more, which comprises preparing an aluminosilicate gel, generally heating it to a temperature of 260° + 60°F, preferably heating it to at least 220°F, adding an alkyl ammonium compound (e.g., tetrapropyl ammonium bromide) or precursors therefor, to the gel in such manner that only nucleating-inhibiting concentrations thereof exist during crystallization, and thereafter raising the temperature of the mixture to 320 ± 100°F, preferably at least 300°F, to promote crystallization.

The term large crystal is a relative term defined herein to include crystals having a diameter in excess of 1 micron, e.g., of from 1 to 2 microns or more. Such crystal size has proven advantageous for ZSM-5 type catalysts useful in hydroconversion processes. For example, as mentioned hereinabove ZSM-5 catalysts comprising crystals of such size are highly useful in selective toluene disproportionation and methanol conversion processes.

Zeolites prepared by the process of the present invention are exemplified by ZSM-5, ZSM-11, ZSM-12, ZSM-35, ZSM-38, and other similar materials. As noted hereinabove, U.S. Patent 3,702,886 describes and claims ZSM-5.

ZSM-11 is more particularly described in U.S. Patent 3,709,979.

ZSM-12 is more particularly described in U.K. Patent Specification 1,365,317.

ZSM-35 is more particularly described in U.S. Patent 4,016,245.

ZSM-38 is more particularly described in U.S. Patent 4,046,859.

The organic component employed in preparing the large size zeolite crystals in accordance with this invention is selected from alkyl ammonium compounds and more particularly from quaternary compounds, (preferably from C₁-C₁₀ alkyl ammonium compounds and ions thereof, especially from tetra-alkyl halogenated ammonium compounds, such as tetra-methylammonium or tetrapropylammonium bromide). Furthermore,

instead of the alkyl ammonium compound itself, precursors thereof may also be advantageously used. In the case of tetra-*n*-propylammonium bromide, tri-*n*-propylamine and *n*-propyl bromide may be used.

5 The method of preparation of the instant large crystal catalysts incorporates techniques 5
to inhibit nucleation of the aluminosilicate zeolite while promoting crystal growth from the
crystallization reaction mixture. Specifically, the technique utilizes the fact that crystal
growth is promoted by higher temperatures and nucleation is promoted by high
concentrations of the quaternary or other organic compound essential to the crystallization
10 of the zeolite. One method that successfully produces large aluminosilicate zeolite crystals 10
is to prepare the aluminosilicate gel without the necessary organic component, heat to an
elevated temperature, or within the range of $260 \pm 60^\circ\text{F}$ usually $>220^\circ\text{F}$, then introduce the
organic compound in controlled, nucleating-inhibiting, concentrations or in such a manner
that only nucleating-inhibiting concentrations of the organic compound effectively exist at
15 any time during the crystallization, and then raise to a crystallization temperature to within 15
the range of $320 \pm 100^\circ\text{F}$, usually $>300^\circ\text{F}$. Another method of controlling the organic
concentration which is a preferred embodiment is to introduce a mixture of the precursor
materials for the organic compound synthesis, e.g., for tetrapropylammonium bromide,
tri-*n*-propylamine and *n*-propyl bromide, to the aluminosilicate gel at the elevated
20 temperature and under conditions of agitation and controlled crystallization temperature. 20
The high agitation (generally from 90-140 rpm) disperses the organic precursors uniformly
throughout the mix in such a way that reaction to form the quaternary compound is
inhibited; therefore, a uniform nucleating-inhibiting concentration of the quaternary is
maintained throughout the crystallization. The quaternary compound (i.e., alkyl ammo-
nium compound, or the precursor materials) can be introduced during or before
25 crystallization. Also, the alkyl ammonium compound can be introduced at the crystalliza- 25
tion temperature and/or at small controlled rates.

The high temperature preparations in the following three tables demonstrate the effect of
concentration of the essential organic species. The concentration has been varied by
replacement of tetra-*n*-propylammonium bromide with its precursors, tri-*n*-propylamine
30 and *n*-propyl bromide, and limiting the extent of reaction by agitation. In said Tables 1 and 30
2 as well as Table 4 the crystal size is given in terms of the large dimension of the respective
crystal while in Table 3 crystal size is given in terms of the crystals large and small
dimensions.

35 TABLE 1 35
High concentration of organic species and variable agitation

Examples 1, 2 and 3 are normal preparations of ZSM-5 using the quaternary salt,
tetra-*n*-propylammonium bromide. There is no difference in crystal size as agitation is
varied since concentration of the nucleating species remains the same. Example 4
40 demonstrates the capability of reacting the quaternary precursors in the presence of 40
methylethyl ketone to produce a significant concentration of the nucleating species. A
quiescent period of time was required for reaction of the precursors.

TABLE 1
High concentration of organic species
variable agitation

5	Example No.	1	2	3	4	5
10	Mole Ratio of Charge (Basis: 1.0 mole Al_2O_3)					10
	Al_2O_3	1	1	1	1	
	SiO_2	94	94.0	94.0	94	
	Na	181	181	181	181	
15	Tri- <i>n</i> -propylamine	-	-	-	9.19	15
	<i>n</i> -propyl bromide	-	-	-	9.19	
	Methylethyl ketone	-	-	-	30.2	
	TPA Br	9.17	9.17	9.16	-	
	H_2O	3880	3880	3880	3890	
20	Crystallization Data					20
	Prereaction					
	Temp. °F	-	-	-	260	
	Time Hr	-	-	-	14	
25	Agitation RPM	-	-	-	0	25
	Crystallization					
	Temp. °F	316	317	321	320	
	Time Hr	<21	<8	<16	<9	
30	Agitation RPM	76	121	121	167	30
	Mole Ratio of Product (Basis: 1.0 mole Al_2O_3)					
35	Al_2O_3	1	1	1	1	35
	SiO_2	70.4	72.5	75.0	72.5	
	Na_2O	0.62	0.71	0.55	0.59	
	N_2O	1.17	1.30	1.23	1.16	
	C	34.3	30.9	34.7	34.3	
40	C/N Ratio ($\text{Na}_2\text{O} + \text{N}_2\text{O}$)/ Al_2O_3	14.7	11.9	14.1	14.8	40
		1.78	2.01	1.78	1.75	
	Nitrogen Content, Liquor Wt. %	.10	0.11	.09	.02	
45	Crystal Size μ	~.1 est	~.1 est	~.1 est	~.1 est	45

50 TABLE 2

Low concentration of organic species and low agitation

55 Examples 5, 6 and 7 produced larger crystals than were attained by preparations shown in Table 1. The larger crystals resulted from a low concentration of the organic species necessary for nucleation. The low concentration, caused by limiting reaction of the precursors by agitating the mixture, is demonstrated by the low nitrogen content of the mother liquor. Although this agitation was not severe enough to disperse the organic precursors throughout the mix, the effect on precursor reaction is apparent when Example 7 is compared with Example 4. Example 7 resulted in crystals of greater than about 1 micron while Example 4 produced crystals with dimensions of only about 0.1 micron. This was due to the lower effective concentration of the organic species in Example 7 as verified by the low nitrogen content of the mother liquor after crystallization.

65 TABLE 3

Low concentration of organic species and high agitation

A higher degree of agitation than that employed by Example 5-7 was employed during

preparation of Examples 8, 9, 10, 11 and 12. This degree of agitation resulted in increased dispersion of the precursors and generally larger crystals than those attained with a lower degree of agitation. Clearly the data of Table 3 shows that large crystals can be readily obtained by low concentration of the organic species with high agitation.

TABLE 2
Low concentration of organic species -
low agitation

Example No.	5	6	7
Mole Ratio of Charge (Basis: 1.0 mole Al_2O_3)			
Al_2O_3	1.0	1.0	1.0
SiO_2	94.0	94.0	94.0
Na	181	181	181
Tri- <i>n</i> -propylamine	9.17	9.17	9.19
<i>n</i> -Propyl bromide	9.17	9.17	9.19
Methylethyl ketone	-	-	30.2
TPA Br.	-	-	-
H_2O	3880	3880	3890
Crystallization Data			
Prereaction			
Temp. °F	-	-	-
Time Hr	-	-	-
Agitation RPM	-	-	-
Crystallization			
Temp. °F	318	319	316
Time Hr.	<20	<13	<18
Agitation RPM	76	76	76
Mole Ratio of Product (Basis: 1.0 mole Al_2O_3)			
Al_2O_3	1.0	1.0	1.0
SiO_2	74.5	70.7	67.8
Na_2O	0.29	0.20	0.40
N_2O	1.38	1.31	0.95
C	26.1	25.2	22.5
C/N Ratio ($\text{Na}_2\text{O} + \text{N}_2\text{O}$)/ Al_2O_3	9.48	9.64	11.8
	1.66	1.52	1.35
Nitrogen Content, Liquor Wt. %	.003	.001	.001
Crystal Size μ	>1	>1	>1

The effect of temperature on rate of crystal growth is shown in Table 4. Both preparations employed tetra-*n*-propyl ammonium bromide. Example 15, crystallized at 210°F required 192 hours and produced crystals less than 0.05 micron in diameter. Crystallization of Example 14, a substantially identical reaction mixture at 317°F resulted in crystals of at least twice that size (~.1 micron).

TABLE 3
Low concentration of organic species - high agitation

Example No.	8	9	10	11	12
Mole Ratio of Charge (Basis: 1.0 mole Al_2O_3)					
Al_2O_3	1	1	1	1	1
SiO_2	94.0	94.0	94.0	94.0	94.0
Na	181	181	181	181	181
Tri- <i>n</i> -propylamine	9.17	9.17	9.17	9.17	9.17
<i>n</i> -Propyl bromide	9.17	9.17	9.17	9.17	9.17
Methylethyl ketone	-	-	-	30.2	30.2
TPA Br.	-	-	-	-	-
H_2O	3880	3880	3880	3880	3880
Crystallization Data					
Prereaction					
Temp. °F					
Time Hr.					
Agitation RPM					
Crystallization					
Temp. °F	320	320	320	320	320
Time Hr.	<14	<17	<18	<17	<17
Agitation RPM	121	121	121	121	121
Mole Ratio of Product (Basis: 1.0 mole Al_2O_3)					
Al_2O_3	1	1	1	1	1
SiO_2	70.3	74.4	71.5	76.8	71.9
Na_2O	0.35	0.31	0.25	0.30	0.29
N_2O	0.79	1.13	1.33	1.17	1.08
C	15.5	21.9	26.2	27.3	25.2
C/N Ratio ($\text{Na}_2\text{O} + \text{N}_2\text{O}$)/ Al_2O_3	9.78 1.14	9.69 1.44	9.88 1.58	11.7 1.47	11.7 1.37
Nitrogen Content, Liquor Wt. %	.001	< .001	< .001	< .001	< .001
Crystal Size μ	^A ~3-5 ^B ~1-2	~3-5 ~1-2	~3-4 ~1	~3-4 ~1-2	~3-5 ~1-2

^A Large dimension of crystal

^B Small dimension of crystal

TABLE 4
Effect of crystallization temperature

5	Example No.	14	15	5
	Mole Ratio of Charge (Basis: 1.0 mole Al_2O_3)			
10	Al_2O_3	1	1	10
	SiO_2	94.0	99	
	Na	181	162	
	Tri-n-propylamine	-	-	
	n-propyl bromide	-	-	
15	Methylethyl ketone	-	-	15
	TPA Br	9.17	9.68	
	H_2O	3880	4096	
	Crystallization Data			
20	Crystallization			20
	Temp. °F	317	210	
	Time Hr	<8	192	
25	Mole Ratio of Product (Basis: 1.0 mole Al_2O_3)			25
	Al_2O_3	1	1	
	SiO_2	72.5	73.9	
	Na_2O	0.71	0.87	
30	N_2O	1.30	1.32	30
	C	30.9	-	
	C/N Ratio	11.9	-	
35	$(\text{Na}_2\text{O} + \text{N}_2\text{O})/\text{Al}_2\text{O}_3$	2.01	2.18	35
	Nitrogen Content, Liquor Wt. %	0.11	-	
40	Crystal Size μ	~.1 est	<.05	40

WHAT WE CLAIM IS:

1. A process for preparing a crystalline aluminosilicate zeolite characterized by having at least one crystalline dimension of 1 micron or more which comprises preparing an aluminosilicate gel, and then adding an alkyl ammonium compound or precursors thereof to the gel under conditions such that only nucleation-inhibiting concentrations of said compound exist during crystallization and thereafter raising the temperature of the mixture to $320 \pm 100^\circ\text{F}$ to promote crystallization.
2. The process of claim 1 wherein the alkyl ammonium compound consists of C_1 - C_{10} alkyl ammonium compounds or ions thereof.
3. The process of claim 2 wherein said alkyl ammonium compound is a tetraalkyl halogenated ammonium compound.
4. The process of claim 3 wherein said ammonium compound is tetra-n-propyl ammonium bromide.
5. The process of claim 4 utilizing the following precursor materials of tetra-n-propylammonium bromide: tri-n-propylamine and n-propyl bromide.
6. The process of any of claims 1 to 5 wherein the aluminosilicate gel is heated to an elevated temperature of from $260^\circ \pm 60^\circ\text{F}$ prior to adding the alkyl ammonium compound.
7. The process of claim 6 wherein said elevated temperature is at least 220°F .
8. The process of any of claims 1 to 7 wherein said crystallization temperature is at least 300°F .
9. The process of any of claims 1 to 8 wherein said zeolite has at least one crystalline dimension greater than 2 microns.
10. The process of claim 9 wherein said crystalline dimension is from about 3-5 microns.
11. The process of any of claims 1 to 10 wherein the concentration of the alkyl

ammonium compound is controlled by introducing a mixture of the precursor materials to the aluminosilicate gel at an elevated temperature under agitation of from 90 to 150 RPM.

12. The process of any of claims 1 to 11 wherein the alkyl ammonium compound or the precursor materials are introduced to the crystallization medium under agitation prior to crystallization.

13. The process of any of claims 1 to 11 wherein the alkyl ammonium compound or precursor materials are introduced under agitation during crystallization.

14. The process of claim 12 or 13 wherein the agitation is at least 90 RPM.

15. A process of preparing a crystalline aluminosilicate zeolite according to Claim 1 substantially as described in any one of the foregoing Examples 5 to 12.

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FIGURE 1
EFFECT OF PARTICLE SIZE ON AGING

